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Proton and deuteron field-cycling NMR relaxometry of liquids confined in porous glasses

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Abstract

Polar and non-polar liquids in porous glasses have been studied by proton and deuteron field-cycling NMR relaxometry. The mean pore diameters were 4 nm, 30 nm and 208 nm. The frequency dependence of the spin-lattice relaxation time T1 is strongly influenced by the polarity of the adsorbate. Non-polar liquids show a flat T1 dispersion compared with polar species. We designate the two cases as 'weak' and 'strong' adsorption respectively. Molecules of liquids at surfaces are known to adopt a preferential orientation, whereas they retain a high diffusivity. Therefore, reorientations mediated by translational displacements (RMTD) must contribute to the correlation function which decays on a timescale of up to eight orders of magnitude greater than in the bulk. The high diffusivity at the surface is made plausible by a mechanism called bulk-mediated surface diffusion recently proposed by Bychuk and O'Shaughnessy [O.V. Bychuk and B. O'Shaughnessy, J. Chem. Phys., 101 (1994) 772]. These authors found that the displacements effective on the surface can be described as the result of Levy walks. They therefore obey a Cauchy distribution. This work employs the Cauchy distribution for a numerical derivation of a surface correlation function, g(r/c), which correctly reproduces the typical correlation lengths of the substrate and thus renders the notion of the liquid molecules performing Levy walks reasonable. The difference in T1 dispersion behaviours of polar and non-polar adsorbates disappears when the free liquid is frozen while the approximately two monolayers thick surface film remains liquid. The T1 dispersions are then equally steep irrespective of the polarity. This indicates that a non-polar liquid confined to a thin, topologically two-dimensional layer on a polar surface undergoes the same relaxation mechanism as a strongly adsorbed polar liquid which is dominated by RMTD processes. | Polar and non-polar liquids in porous glasses have been studied by proton and deuteron field-cycling NMR relaxometry. The frequency dependence of the spin-lattice relaxation time T1 is strongly influenced by the polarity of the adsorbate. Non-polar liquids show a flat T1 dispersion compared with polar species. The difference in T1 dispersion behaviors of polar and non-polar adsorbates disappears when the free liquid is frozen while the approximately two monolayers thick surface film remains liquid. The T1 dispersions are then equally steep irrespective of the polarity. This indicates that a non-polar confined to a thin, topologically two-dimensional layer on a polar undergoes the same relaxation mechanism as a strongly adsorbed polar liquid dominated by RMTD processes.

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Keywords

deuteron field-cycling NMR relaxometry, non-polar liquids, polar liquids, porous glasses, proton field-cycling NMR relaxometry